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Dications possess unusual electronic structures and bonding configurations. They display high energy releases and thus may serve as prototypes for molecular systems which have enormous energy per unit mass. This program combines a parallel experimental and theoretical approach to the study of gaseous molecular dication species. This includes spectroscopy, kinetics and reactions, and high level electronic structure calculations. Broad survey calculations with complete active space self-consistent field (CAS-SCF) wavefunctions have been carried out to characterize many of the hydride, fluoride, and oxide dication species. Highly accurate multireference configuration interaction (MR-CI) wavefunctions have established the electronic structures and stabilities of species such as CF^{2+} , F_2^{2+} , HS^{2+} , NF^{2+} , N_2^{2+} , C_2^{2+} , and PH^{2+} . Vibrational and rotational constants,

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"Multireference configuration interaction (MR-CI) calculations on HS^{2+} and experimental observation via electron impact ionization of H_2S ," P. J. Miller, S. A. Rogers, J. Senekowitsch, S. V. O'Neil, S. R. Leone, H.-J. Werner and P. J. Knowles, Int. J. Mass Spectrom. Ion Proc. 100, 505 (1990).

"Ab initio calculation of the $X^2\sigma^+$ and $A^2\pi$ states of CF^{++} ," J. Senekowitsch, S. V. O'Neil, H.-J. Werner and P. J. Knowles, J. Chem. Phys. 93, 562 (1990).

"Low-lying electronic states of PH^{2+} ," J. Senekowitsch, S. V. O'Neil, H.-J. Werner and P. J. Knowles, Chem. Phys. Lett. 175, 548 (1990).

"Ab initio characterization of NF^{2+} ," J. Senekowitsch, S. V. O'Neil, H.-J. Werner and P. J. Knowles, J. Phys. B 24, 1529 (1991).

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"Spin-forbidden decay of the dication HS^{++} ," G. Parlant, J. Senekowitsch, S. V. O'Neil, and D. R. Yarkony, J. Chem. Phys. 94, 7208 (1991).

"The $^3\pi_g$ from $^3\sigma_u^+$ transition in N_2^{++} ," J. Senekowitsch, S. V. O'Neil, P. J. Knowles and H.-J. Werner, J. Phys. Chem. 95, 2125 (1991).

"Metastable $^3\sigma_g^-$ ground state of F_2^{++} and the bonding in molecular dications," J. Senekowitsch and S. V. O'Neil, J. Chem. Phys. 95, 1847 (1991).

"Characterization of triplet states in doubly charged positive ions: Assignment of the $^3\pi_g$ from $^3\sigma_u^+$ electronic transition in N_2^{2+} ," D. M. Szaflarski, A. S. Mullin, K. Yokoyama, M. N. R. Ashfold and W. C. Lineberger, J. Phys. Chem. 95, 2122 (1991).

9. Abstract of Objectives and Accomplishments:

Dications possess unusual electronic structures and bonding configurations. They display high energy releases and thus may serve as prototypes for molecular systems which have enormous energy per unit mass. This program combines a parallel experimental and theoretical approach to the study of gaseous molecular dication species. This includes spectroscopy, kinetics and reactions, and high level electronic structure calculations. Broad survey calculations with complete active space self-consistent field (CAS-SCF) wavefunctions have been carried out to characterize many of the hydride, fluoride, and oxide dication species. Highly accurate multireference configuration interaction (MR-CI) wavefunctions have established the electronic structures and stabilities of species such as CF^{2+} , F_2^{2+} , HS^{2+} , NF^{2+} , N_2^{2+} , C_2^{2+} , and PH^{2+} . Vibrational and rotational constants, tunneling lifetimes, and transition strengths are obtained, providing guidance to the experimental studies. Reactive studies have been carried out in a crossed beam arrangement on CO^{2+} , NO^{2+} , and HCl^{2+} with rare gases and hydrogen. Selective product channels are observed and cross sections obtained. High resolution laser spectroscopy of the $^3\pi_u - ^3\pi_g$ transition in N_2^{2+} has been obtained in a coaxial laser/beam apparatus by monitoring the threshold appearance of predissociated fragments. Detailed vibrational and rotational constants are obtained.

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Motivation for Studies of Dication Species

Doubly charged molecular ions are novel species with unique energetic and bonding properties.¹⁻⁷ As a class, they can exhibit high energy content, long lifetimes against predissociation, and bonding partnerships for which there are no neutral analogs. Intuition might suggest that the coexistence of two positive charges in one molecule might be feasible provided the charges can be spatially separated and mutually shielded from one another. Hence it is not surprising that an extended species such as $\text{CH}_2\text{CCCCH}_2^{2+}$ is stable.⁵ However, much more compact dication species, such as diatomics, also exist and possess a number of exceptional properties. For example, He_2^{2+} is known to be a long-lived metastable species⁶ trapped in a 1.5 eV potential well, which upon dissociation to 2 He^+ releases 20.5 eV of Coulomb repulsion energy. The list of such diatomic and small polyatomic dication species is not short, and in our own work, we have already observed NF^{2+} , CF^{2+} , HCl^{2+} , NO^{2+} , CO^{2+} , N_2^{2+} , CCl^{2+} , HCCl^{2+} , $\text{H}_2\text{CCl}^{2+}$, CF_2^{2+} , CF_3^{2+} , NF_2^{2+} , H_2S^{2+} , and H_3S^{2+} .

Ion systems in general have considerable potential to increase the specific energy content of propellant systems compared to the standard hydrogen/oxygen fuel. A brief survey of ion exoergicities shows that even the simplest ion-ion recombination process, for example $\text{H}^+ + \text{O}^-$, can release 16.5 eV of energy, compared

to 2.5 eV from the reaction of $\text{H}_2 + 1/2 \text{O}_2$ to form water. The combination of high energy content and small mass makes simple dications compelling candidates for high specific energy content systems. While dication species are for the most part metastable, the prospect of trapping substantial energy in a single molecular vibrational mode and releasing it with a mechanism that initiates predissociation presents intriguing possibilities. We believe that future searches for potentially energetic species will include doubly charged molecular ions, and that species such as those listed above represent prototype "core" electronic configurations which warrant further exploration both theoretically and experimentally. Dications exhibit bonding partnerships for which there are no neutral analogs, and experiments to learn how to control their stability and the release of their energy will be of fundamental importance.

In order to utilize ion species in propellant technology, experiments and theory will have to address a wide variety of complex topics. These include the limits of Coulomb explosion of multiply charged particles, tunneling through barriers for both heavy particles and electrons, encapsulation and trapping of ions in solids and low temperature slushes (e.g. hydrogen), the utilization of counter ions for electrical neutrality in trapping, stabilization of charges with membranes, pressure effects on particle mobility in solids, growth of low temperature crystals in which species are controlled to occupy designated sites, basic collision physics and chemistry, reaction pathways and energetics, methods to prepare large quantities of ions, and fundamental structures and stability of novel high energy species. Understanding the conceptual physics and chemistry of these species will be an

important step toward identification of realistic high energy density materials. Toward this end, investigation of molecular dications must center first on the electronic structures and binding mechanism of the highly repulsive charged particles, the dynamics of dissociation, tunneling through barriers, and the reactive properties of these species.

Theoretical Characterization of Dications

ONeil has carried out broad *ab initio* CAS-SCF surveys of several classes of interesting diatomic dications and then selected several species for accurate MR-CI examination. A brief summary of the general findings is given below, followed by a sampling of specific results.

The first theoretical goal of the project was identification of a suitable family of systematic basis sets. After testing several alternatives, we discovered Dunning's recently published correlation consistent valence triple zeta (cc-VTZ) sets⁸ to be an excellent choice. For first row atoms, these sets contract to $4s, 3p, 2d, 1f$ and so already include compatible polarization functions appropriate for correlating the valence shell. These sets are particularly appropriate since they were optimized in a correlated environment similar to the one in which they were deployed here. Original concerns that the tighter orbitals in doubly charged species might require relaxation of contracted basis sets designed for neutral atoms proved unnecessary; our tests with the cc-VTZ basis showed that multireference CI from a CAS-SCF reference function reproduced term values for neutral, singly, and doubly charged first row atoms to within 2%. But basis augmentation was indeed necessary to

account for the outer orbital deformation that governs the long range induction and dispersion terms, both of which are proportional to the dipole polarizability. With MR-CI wavefunctions, well-tempered extension of the cc-VTZ *s*, *p*, *d*, and *f* spaces by a single diffuse function each reproduced the polarizability of atomic neon to 5%, fully meeting the current requirements.

Using these cc-VTZ-diffuse bases, the usual theoretical procedure was to perform a restricted Hartree-Fock on an electronic state selected for its single-configuration character, then freeze the K-shell orbitals while optimizing the valence orbitals in a state-averaged CAS-SCF procedure. For qualitative work the CAS-SCF results themselves sufficed. For quantitative studies, the CAS-SCF multiconfiguration wavefunctions were used as reference functions in a multi-reference singles and doubles CI.

After establishing these preliminary procedures, the first calculations directed toward examining the existence and properties of dications were CAS-SCF surveys of the first and second row diatomic hydrides and the first row oxides. We give them here only in summarized form.

Our early survey of first row oxides uncovered a number of quasi-bound systems, but facile experimental access to these species meant most were known from other groups or became so during our work.⁹⁻¹¹ Given the flourish of measurements on the first row oxides, we did not pursue that direction theoretically. The class is not exhausted, however, and fruitful work remains to be done on the electronically excited states.

The first row diatomic hydrides show little tendency to form quasi-bound dications. This may be because the spatially compact L-shell orbitals form a bond only at distances short enough to produce an insurmountable Coulomb repulsion of the constituent nuclei. One strong exception is BeH^{2+} ,¹² which exhibits a strong well in the $^2\Sigma^+$ symmetry with the lowest vibrational level about three eV above the asymptote.²

Perhaps because the greater spatial extent of the M-shell orbital permits bond formation at somewhat longer distances, the second row hydrides form quasi-bound dications readily, with MgH^{2+} , AlH^{2+} , SiH^{2+} , PH^{2+} , SH^{2+} , and ClH^{2+} developing wells deep enough to trap several vibrational levels.¹³⁻¹⁹ We have performed and published detailed MR-CI studies and vibrational analyses on two of these species, PH^{2+} and SH^{2+} , the latter in parallel with the measurements of Leone. One interesting trend is that even though hydrogen tunnels with impunity in more typical chemical systems, the lifetimes of the $v=0$ levels in the quasi-bound dications are essentially infinite. The explanation rests partly with barrier height and partly with an atypical barrier width, the outer limb falling off only as $1/R$ rather than the $1/R^6$ appropriate to the potentials of most neutrals. The accurate MR-CI studies of SH^{2+} and PH^{2+} have been published.¹⁶⁻¹⁸

In carrying out the surveys described above, we developed several numerical tools useful for all subsequent work. Among these were techniques for automated application of the Wigner-Witmer rules to list and graphically display the molecular symmetries from constituent atom asymptotic symmetries, a treatment of oscillator strength matrix elements consistent for true bound states that

are square-integrable and resonance states that are not, procedures to isolate resonance positions and determine their widths precisely, and standard operating procedures for state-averaged CAS-SCF to deal with the numerous interacting states that must be considered in dications.

With these tools in place, we examined the next promising class of dications, the first row diatomic fluorides. The particulars of each naturally differ, but CF^{2+} will serve as an apt example because fluorocarbon precursors suggest ready study of this species in the laboratory component of this project.

Exploratory state-averaged full valence CAS-SCF calculations on CF^{2+} including all doublet states arising from the $^2\text{P}_u(\text{C}^+) + ^3\text{P}_g(\text{F}^+)$ asymptote showed the $\text{X}^2\Sigma^+$ and $\text{A}^2\Pi$ states possess deep quasi-bound potential wells, and reveal inflection points in the potential energy curves of the $^2\Delta$, $2^2\Pi$, and $1^2\Sigma^-$ states. The existence of another metastable doublet state correlating with the lowest asymptote cannot be ruled out from these calculations. However, as indicated by the CAS-SCF calculations such a state would lie at least 1.5 eV above the top of the barrier of the $\text{X}^2\Sigma^+$ state. The quartet states were not considered in this work since their high spin is inauspicious for bonding.

The MR-CI potential energy curves of the $\text{X}^2\Sigma^+$ and $\text{A}^2\Pi$ states were calculated at 18 internuclear distances between 1.6 and 10.0 Bohr. Beyond a distance of about 8 Bohr the potentials revert to a Coulomb repulsion between C^+ and F^+ . At bonding distances the situation is similar to the known NO^{2+} ,¹⁰ with a shallow $^2\Pi$ well lying above a much deeper $^2\Sigma^+$ well. The electronic character at the well minima was $\text{C}^{2+}-\text{F}$, consistent with the avoided crossing picture presented in the

introduction. Spectroscopic constants derived from a Dunham analysis were also obtained. Preparation of CF^{2+} by a vertical double ionization from the neutral CF ($X^2\Pi$) molecule in $v = 0$ ($R_e = 2.4$ Bohr) will produce predominantly CF^{2+} in the $X^2\Sigma^+$ ground state with vibrational quanta of $v = 2$ and 3.

The lifetime of the quasi-bound levels of CF^{2+} will be determined by a number of mechanisms, not all of which may be important for each level. Vibrational relaxation by infrared emission, electronic relaxation $\Sigma \leftarrow \Pi$ and $\Pi \leftarrow \Sigma$ (for high v), and tunnelling all play a part, with the net lifetime given by the usual reciprocal sum $1/\tau_{\text{tot}} = 1/\tau_v + 1/\tau_e + 1/\tau_t$. Bound-resonance-continuum transitions within and between the two electronic states were calculated by numerical integration. Tunneling lifetimes were first estimated from a WKB approximation and then calculated precisely from quantum mechanical scattering calculations which extracted the resonance width from a Lorentzian fit to the phase shifts as a function of energy. We obtain the total lifetimes of each vibrational level in the various electronic states, as well as the contributions of τ_v , τ_e , and τ_t . The tunneling lifetime of the $v=0$ level in the $^2\Sigma^+$ state is long beyond computation and the other two decay processes are inapplicable, so this level is essentially stable for the isolated dication. Higher levels in either electronic state have finite lifetimes, but some are well beyond the minimum necessary for the companion laboratory studies.

In addition to the previously mentioned hydride publications, multireference-CI calculations similar to those described above for CF^{2+} have been carried out for NF^{2+} (for which measurements from Leone's laboratory are described below), and for C_2^{2+} , N_2^{2+} , and F_2^{2+} .²³ Rather than present full detail for these four

systems, we summarize some key features of the last two. In F_2^{2+} , we have found the $X^3\Sigma^-$ ground state lying over 7 eV above the $F^+ - F^+$ asymptote and possessing a well supporting four quasi-bound vibrational levels. Hurley⁷ included F_2^{2+} in his 1961 semi-empirical study, but to our knowledge this is the first high accuracy calculation reported for this state. Analysis of the theoretical potential yields $R_e = 1.289 \text{ \AA}$, $\omega_e = 919.4 \text{ cm}^{-1}$, $\omega_e x_e = 16.31 \text{ cm}^{-1}$, and $B_e = 1.073 \text{ cm}^{-1}$. Because the well is so shallow, even the $v=0$ lifetime is only about 16 msec but this should allow experimental detection and spectroscopic analysis.

Determining the electronic states of N_2^{2+} proved challenging because of the numerous states lying between the $N^+ - N^+$ and the $N - N^{2+}$ asymptotes.²⁴ Many could be omitted safely, and other studies have examined special states in this system,^{25,26} but we characterized more electronic states than usual because the motivation for studying this system in the first place was to help with the assignment of unidentified bands in a very high resolution N_2^{2+} spectrum obtained in Lineberger's laboratory. Extensive use of the Kirtland Cray II was essential here, and the theoretical analysis provided substantial guidance in assigning the measured spectrum discussed below.

A common finding in the systems we have investigated theoretically so far is that while CAS-SCF remains the tool of choice for our survey studies and gives good approximations to R_e , it is not reliable as a predictor of the position and height of the potential barrier in dications. For example, in the $X^2\Sigma^+$ and $A^2\Pi$ potentials of CF^{2+} , the CAS-SCF $X^2\Sigma^+$ potential would be acceptable but the corresponding $^2\Pi$ potential, while revealing a well, poorly estimates the position

and depth. The MR-CI calculation was necessary. This trend heightens a concern first expressed by Taylor.²⁴ The inability of CAS-SCF to deliver accurate information about barrier heights is serious because of the impact of barrier height on tunnelling lifetimes, one of the characteristics central to the current study. In practice, this requires that data shared with the collaborative experimental efforts must be derived from MR-CI wavefunctions.

With the knowledge gained from the work completed, and specifically from the state-averaged CAS-SCF calculations, we can refine the simplest picture that quasi-bound dications arise from an avoided crossing between a repulsive Coulomb potential from the lowest $A^+ + B^+$ asymptote and an attractive polarization potential of the same symmetry from the $A + B^{2+}$ charge-transfer asymptote. This is really only an approximation in that typical diatomics have numerous intervening electronic states with a symmetry matching that of the idealized avoided crossing pair. In fact, one conclusion from the theoretical work is that potential curves of diatomic dications are best thought of as the sum of an ordinary chemical binding between $A^+ + B^+$ and a Coulomb repulsion of the constituent ions: $V(R) = V_{\text{bond}}(R) + e^2/R$, giving the high-lying well-and-barrier combination typical of these species and explaining why accurate *ab initio* calculation of dications requires substantially more effort than isoelectronic neutrals. Keeping a balance between the repulsive e^2/R term, recovered in full even in crude calculations, and the chemical binding portion of the interaction, suffering the common correlation error, requires an unusually complete recovery of $V_{\text{bond}}(R)$, possible only with large basis sets and highly correlated wave functions.

From our systematic surveys and from the work of others⁷⁻²⁷ it has become clear that quasi-bound dications are fairly common. The pointed questions now become how can they be manipulated in isolation – i.e. what are their detailed properties – and how do they interact with neutral species that might serve as candidates for matrices?

Laboratory Investigations of Dication Formation and Collisions

Laboratory investigations were carried out to explore the formation, spectroscopy, and stability of many of the dication species which are predicted by ONeil's calculations. In studies by Leone, a novel ion source has been developed to produce beams of mass selected dications for collision studies and for broad spectral surveys. This ion source is coupled to a crossed beam collision apparatus which has subsequent time-of-flight (TOF) detection of product ions.

The ion source region^{17,28} consists of a pulsed valve to introduce the reagent gas into the ionizer section, an electron beam ionizer, a quadrupole mass spectrometer, and focusing lenses to collimate the beam. The dication ion beam is subsequently crossed with a jet of target gas, and the primary ions and product ions are pulse-extracted at a right angle into the TOF mass spectrometer. By using suitable isotopes in the precursor molecules, doubly charged molecular ions are definitively assigned to the half-mass peaks transmitted by the quadrupole mass filter.

With this apparatus, a large number of dication species have been formed by crossing the electron beam with various precursor reagents. For example, we can

form NO^{2+} , CO^{2+} , N_2^{2+} , and HCl^{2+} from selected isotopes of NO, CO, N_2 , and HCl, respectively, NF^{2+} and NF_2^{2+} from NF_3 , CCl^{2+} and $\text{H}_2\text{CCl}^{2+}$ from CH_3Cl , CF^{2+} , CF_2^{2+} , and CF_3^{2+} from CF_4 , and HS^{2+} and H_3S^{2+} from H_2S , the latter presumably due to ion reactions in the source region.

Typically, the doubly charged molecular ions are a few percent of the singly charged ion yields, both in our investigations and in previous reports using electron impact ionization.²⁹ The dication yields using electron impact are sometimes less than can be obtained by charge stripping, especially when extensive fragmentation or production from unstable neutral species is required.^{6,30} However, our apparatus is considerably simpler and provides sufficient ion fluxes for a variety of novel studies.

In our apparatus, the ions are extracted with only a few volts of kinetic energy. Thus, ions with lifetimes of 10 μs or longer will survive all the way to the primary beam detector. Many of the ions under investigation are stable indefinitely without collisions. By applying retarding potentials after the initial extraction through the quadrupole, we are able to lower the kinetic energy of the primary beam even further to study collision processes at near-thermal energies.

We are also able to vary the electron impact energy to obtain appearance threshold energies for specific dication species. Under the assumption that the electron impact double ionization cross section at threshold has a square power dependence upon electron energy,³¹ appearance energies of NF^{2+} were determined from extrapolations of the square root of the double ionization cross section to the

intercept of the electron energy axis. The energy axis was calibrated by comparison to systems with well-known threshold energies.¹⁷

The NF^{2+} dication is formed with two distinct threshold energies; the lowest at 43.8 eV is attributed to the ground electronic state, and the one at higher energy (51.0 eV) is attributed to the existence of an electronically excited state of NF^{2+} . A similar electronically excited state of a dication has been observed³² and calculated²³ for CF^{2+} , and the existence of such states will greatly facilitate Lineberger's high resolution spectroscopic investigations of the structures of these ions. Our first threshold for NF^{2+} appearance, 43.8 eV, is in good agreement with the sum of the measured $\text{NF}_3 \rightarrow \text{NF}^+ + \text{F} + \text{F}$ appearance threshold and the calculated $\text{NF}^+ \rightarrow \text{NF}^{2+} + \text{e}$ ionization energy,³³ which yields 41.4 eV. The partial ionization cross section to form NF^{2+} from NF_3 is also estimated to be 10^{-20} cm^2 by comparison to other known systems run in our apparatus.

Recent experiments of Leone¹⁷ and theoretical calculations of O'Neil and Senekowitsch¹⁷ on HS^{2+} nicely unite our efforts towards developing the predictive capability for dication stability and the ability to verify existence of the ion in the versatile ion source developed here. The observation of a single threshold for the formation of HS^{2+} in the laboratory experiments is in excellent agreement with the theoretical prediction¹⁷ that there is only one bound state of this dication. An added bonus is the observation in the experiments of the formation of H_3S^{2+} , which is formed by ion chemistry in the source region. This result suggests the need for further theoretical investigations to determine whether this ion involves an HS^{2+} ion core bonded to a molecular H_2 or some other structure. If the result is the

former, then we might have a first example of the solvation of a dication by a hydrogen molecule.

The collision portion of Leone's apparatus has recently been used to study a wide range of reactions of CO^{2+} and NO^{2+} with rare gases and hydrogen. Selective channels are observed and a considerable amount of the reactive branching has been obtained. Work in this area is now being prepared for publication.

High Resolution Laser Spectroscopy of Dication Structure and Stability

The mass spectroscopic and reaction kinetic measurements carried out by Leone provide the ability to survey broad classes of dications, yielding important information on reactive stability and formation mechanisms, pointing the way to systems of potential HEDM interest. For selected species, we can then carry out detailed studies of structure and stability using high resolution spectroscopic techniques. The focus of Lineberger's program has been the development of this capability, and the application to simple dication species. We developed a versatile source of dications, made major modifications to a coaxial beam apparatus to enable study of dication photodissociation and obtained high resolution photodissociation spectra of new states of N_2^{2+} .

The apparatus is a high resolution coaxial negative ion-laser beam spectrometer³⁴ converted for positive ion studies and with product detection capabilities modified to enable the detection of ionic photofragments. The various components of the apparatus are described in more detail in the following paragraphs.

The dications are formed by electron impact on an effusive molecular beam. A novel electron gun design³⁵ allows us to obtain fairly high (several mA) electron beam currents very close to the effusive beam aperture, greatly aiding the production of intense dication beams. This ion source has proved capable of generating many small dications, but further modifications will be required to produce intense beams of the H₂-clustered species of possible HEDM interest. Indeed, at this point it is not even certain that such ions can be produced.

The ions are formed into a beam, accelerated and passed through a magnetic sector mass spectrometer with a resolution $M/\Delta M \approx 50$. Following this mass spectrometer, the selected ions pass through an energy analyzing quadrupole field which also serves to merge the ion beam with the coaxial single mode laser beam. Extensive modifications were made to the exit quadrupole deflector to enable detection of the ionic photofragments, fragments which are ejected with significant kinetic energy. The apparatus is basically designed to detect with high sensitivity those fragment ions ejected preferentially along the beam propagation axis. A second 45° electrostatic analyzer further separates the fast, forward scattered photofragments and the slower backward scattered photofragments from the primary dication beam. The forward and backward scattered photofragments strike separate multichannel plate detectors, and time-coincidence detection (1 μ s window) is used to greatly reduce the background from the intense parent ion beam. The design is sufficiently versatile that many different photofragment mass combinations can be detected in coincidence. With further development, it will be possible to use an accurately measured time delay between fast and slow

photofragments to determine quantitatively the energy release upon photofragmentation.

The laser light source is a single mode (or, in some cases, a few modes) high power (0.5 W) tunable laser. For this work, we have supplemented our existing dye laser system (500- 720 nm) with a Ti:sapphire tunable laser which covers the spectral region from 700-1000 nm. This latter wavelength region was badly needed for the dication stability studies, and such a single frequency laser was not available commercially. Taking advantage of tunable laser expertise in JILA, we were able quickly to modify a commercial instrument to provide this new capability.

The initial experiment was to be a study of NO^{2+} photodissociation. Extensive broad band and narrow band searches between 500 and 750 nm failed to reveal any evidence of photodissociation. Since *ab initio* calculations³⁶ indicate that we should expect photodissociation to a continuum state in this region, we are puzzled by the lack of observation of photodissociation signal. While photostability may be attractive for HEDM purposes, the result was disappointing from the point of view of the initial experiment on this apparatus. Following the work on NO^{2+} , we chose to investigate photodissociation of N_2^{2+} , a dication for which Cosby et al.³⁷ and, more recently, Masters and Saare³⁸ have obtained photodissociation spectra.

Detecting the N^+ photofragments in coincidence, we quickly obtained the N_2^{2+} transition previously reported. Subsequent studies were directed toward obtaining information on other N_2^{2+} electron states, and more subtle issues of dication stability.

The previously reported spectra^{37,38} arose from a $^1\Pi \leftarrow ^1\Sigma$ transition, and presented a relatively simple spectrum. Our investigations near $15,000\text{ cm}^{-1}$ showed a much more complex spectrum. In higher resolution, we found over 350 individual lines in this region; this represents far too many lines to be a simple member of the previously reported band system. The detailed analysis of this spectrum was greatly aided by sophisticated electronic structure calculations by Senekowitsch and O'Neil. Their work indicated the strong possibility of a $^3\Pi \leftarrow ^3\Sigma$ transition in the energy range that we observed. Computed bond lengths for the two states gave a very good starting point for recognizing a few progressions. Armed with this information, we began a detailed fitting procedure assuming appropriate selection rules and energy levels for a $^3\Pi \leftarrow ^3\Sigma$ transition. It became apparent that this was indeed a triplet-triplet transition. Further analysis gave an unequivocal confirmation of the assignment. All of the 27 rotational branches possible in such a transition were present in the spectrum and assigned.³⁹

The current state of our knowledge of the electronic states of N_2^{2+} has been summarized in our recent publications. Of particular note is the fact that the spectroscopically analyzed triplet transition is between two excited states. The energy difference between the singlet and triplet states is determined by the accurate calculations of O'Neil and Senekowitsch, as are the overall potential energy curves. Independent experiments by Larsson⁴⁰ have determined the energy release resulting from excitation of the $15,000\text{ cm}^{-1}$ band and confirm the theoretical position (although with less accuracy) of the triplet terms. Both the $^3\Pi \leftarrow ^3\Sigma$ and $^1\Pi \leftarrow ^1\Sigma$ energy difference are calculated at JILA to an accuracy of a few percent. Overall,

these data represent a remarkable example of how well theory and several experiments can interact to produce a complete overall picture of a molecule.

The upper $^3\Pi$ state appears to support only one bound vibrational level, and the shape of the barrier potential is indicative of extensive configuration mixing. Such a state provides a particularly sensitive test of the ability to compute potentials and tunneling lifetimes. Since individual rotational lines are well resolved in the high resolution spectrum, it is possible to obtain lifetimes for this electronic state for various rotational levels. The lifetimes range from 30-50 psec. There is no striking rotational dependence. The observed long lifetime is at variance with the initially calculated lifetime (1 psec), and indicates that unexpected additional states are producing an even larger barrier to dissociation. Refined computations are in progress at present. Further experiments will produce considerably more detailed information on both the lower Σ state, as well as providing increasingly sophisticated tests of the computations of Senekowitsch and ONeil.

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